Factors Affecting Interfacial Electron Transfer of Adsorbed Yeast Cytochrome c at COOH-type Self-Assembled Monolayers

- J. Wallace (Naval Research Laboratory), T. Nahir (California State University), and E. Bowden (North Carolina State University)

In a previous publication, we showed that S. cerevisiae (yeast) cytochrome can be readily adsorbed in an electroactive state on COOH-terminated self-assembled monolayers (SAMs) of the gold/thiol class.[1] Furthermore, it was found that the electron transfer (ET) rates could be manipulated over several orders of magnitude through the use of mixed COOH/OH SAMs. In contrast, horse cytochrome c showed noticeably less dependence (< 10X) on the choice of SAM type, i.e., pure COOH or mixed COOH/OH. Those results were interpreted in terms of variability in electronic coupling at the cytochrome/SAM interface.

In the present paper, we describe some new results for yeast cytochrome c. There are two parts, namely, a more in-depth study of how mixed SAMs can affect ET rates, and a study of the effect of solution pH.

In all cases, the C102T mutant of the iso-1 form of yeast cytochrome c was employed. The C102T mutation is benign with respect to properties of interest while eliminated the possibility of dimerization. The gold electrodes used were evaporated gold films on Ti/glass substrates with an electrochemical pretreatment consisting of anodic cycling in an H_2SO_4/KCl solution.[2]

A series of experiments were conducted with bicomponent mixed SAMs prepared by coadsorption of various combinations of $HS(CH2)_{m=7,10,13}COOH$ and $HS(CH2)_{n=7,10,13}OH$ molecules. The fastest rates obtained were for mixed SAMs in which both COOH and OH were both present and for which m>n. These rates were $>10^3$ higher than a comparable pure COOH SAM of the same length m. The use of mixed SAMs with m=n as well as mixed SAMs containing the same functional group but differing lengths showed substantially slower rates. We hypothesize that these differences in rate are due to differences primarily in electronic coupling. he Pelletier/Kraut[3] model of ET in the cytochrome c / CCP complex may provide valid insight into the differences observed.

The impact of pH on the adsorption and ET kinetics of yeast cytochrome c were examined over the range of 5-9. On pure COOH SAMs, pH had a noticeable effect on ET rate. For a $C_{10}COOH$ SAM, ET rates decreased sigmoidally over three orders of magnitude as the pH was increased from 5-9. We hypothesize that this phenomenon is a direct reflection of the ionization of the COOH SAM over this range, resulting in a highly negative charge at pH 9. How this affects the ET rate is not clear. One possibility is that the resultant strong binding force prevents cytochrome c from achieving an orientation for optimal electronic coupling.

Comparative results for horse cytochrome c will also be presented and discussed.

1. A. El Kasmi, J.M. Wallace, E.F. Bowden, S. Binet, and R.J. Linderman, *J. Am. Chem. Soc.*, **1998**, *120*, 225-226
2. T.M. Nahir and E.F. Bowden, *J. Electroanal. Chem.*, **1996**, *410*, 9-13.
3. H. Pelletier and J. Kraut, Science, 1992, 258, 1748-1755.